Static and dynamical properties of a supercooled liquid confined in a pore[1]

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Abstract. We present the results of a Molecular Dynamics computer simulation of a binary Lennard-Jones liquid confined in a narrow pore. The surface of the pore has an amorphous structure similar to that of the confined liquid. We find that the static properties of the liquid are not affected by the confinement, while the dynamics changes dramatically. By investigating the time and temperature dependence of the intermediate scattering function we show that the dynamics of the particles close to the center of the tube is similar to the one in the bulk, whereas the characteristic relaxation time $\tau_q(T, \rho)$ of the intermediate scattering function at wavevector q and distance ρ from the axis of the pore increases continuously when approaching the wall, leading to an apparent divergence in the vicinity of the wall. This effect is seen for intermediate temperatures down to temperatures close to the glass transition. The ρ-dependence of $\tau_q(T, \rho)$ can be described by an empirical law of the form $\tau_q(T, \rho) = f_q(T) \exp[\Delta_q/(\rho_p - \rho)]$, where Δ_q and ρ_q are constants, and $f_q(T)$ is the only parameter which shows a significant temperature dependence.

1. INTRODUCTION

The dynamics of a bulk liquid in its supercooled state has been investigated extensively in experiments and computer simulations and is understood reasonably well [1,2]. Much less is known about the influence of a spatial confinement on the dynamic properties of a liquid. The growing interest in this topic in recent years is based on the fact that new nanoscale materials with adjustable pore size, such as Vycor glass, have been developed, which allow to study the influence of the confinement. Concerning the details of the glass transition, experiments have so far given controversial results. Depending on the nature of the pores and the contained liquid, some authors report an increase in the glass temperature [3,4], while others find a decrease [5,6]. In this paper we report the results of computer simulations which were done to investigate this phenomenon. Within such simulations (see also [7,8]) it is possible to control the nature of the wall (roughness and wall-liquid interaction), and to do a local analysis of the dynamics of the particles. Therefore this method is well suited to increase our understanding of the effects of the confinement.

2. MODEL AND DETAILS OF THE SIMULATION

To mimic the experimental setup of a fluid confined in porous materials we take as the spatial confinement a cylindrical tube. The contained liquid is chosen to be a simple Lennard-Jones fluid. To prevent crystallization at low temperatures we take a binary mixture of 80% A and 20% B particles with the same mass and interacting via a Lennard-Jones potential of the form $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$ with $\alpha, \beta \in \{A, B\}$ and cut-off radii $r^C_{\alpha,\beta}$=2.5·$\sigma_{\alpha\beta}$. The parameters were chosen as ϵ_{AA}=1.0, σ_{AA}=1.0, ϵ_{AB}=1.5, σ_{AB}=0.8, ϵ_{BB}=0.5, and σ_{BB}=0.88. The bulk properties of this system have been investigated in the past [9]. In the following, all results will be given in reduced units, i.e. length in units of σ_{AA}, energy in units of ϵ_{AA} and time in units of $(m\sigma_{\text{AA}}^2/48\epsilon_{\text{AA}})^{1/2}$. For Argon these units correspond to a length of 3.4Å, an energy of 120Kk_B and a time of $3 \cdot 10^{-13}$s.

To minimize the influence of the changes in *static* properties due to the confinement, such as layering or a change in the static structure factor, on changes in its *dynamic* properties, we chose the wall of the pore

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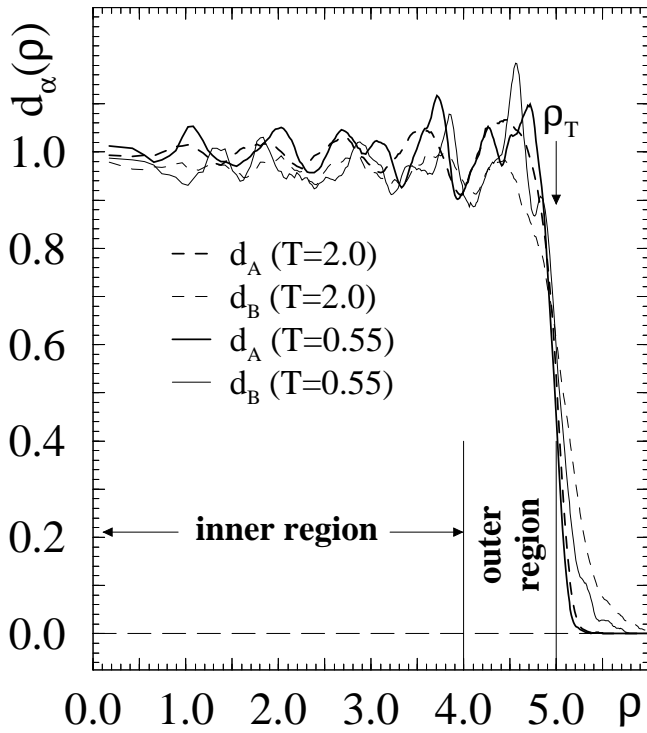[1]Talk presented in the workshop *Dynamics in Confinement* Grenoble, 26 - 29 January, 2000

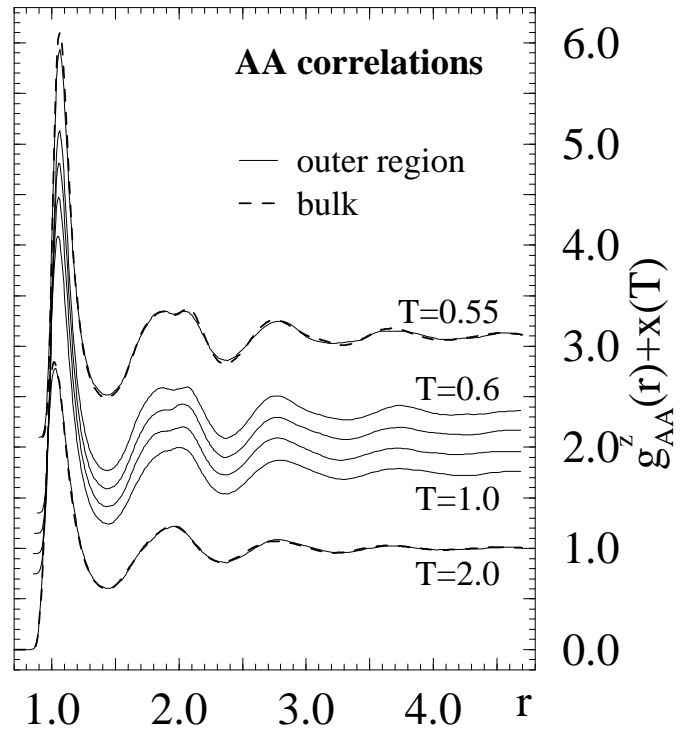**Figure 1.** Density profiles for A and B particles at T=2.0 and T=0.55.

Figure 2. Radial distribution function $g_{AA}^z(r)$ plus vertical offset $x(T)$ in the outer region for T=2.0 (x=0.0), T=1.0 (x=0.75), T=0.8 (x=0.95), T=0.7 (x=1.15), T=0.6 (x=1.35), and T=0.55 (x=2.1); comparison with bulk curves for T=2.0 and T=0.55.

to have an amorphous structure similar to the one of the confined liquid. For this purpose, we equilibrated a large bulk system at an intermediate temperature, T=0.8, and extracted a cylinder with radius $\rho_T + r_{AA}^C$ with a tube radius ρ_T of 5.0. During the simulation of the tube the particles in the outer ring, $\rho \geq \rho_T$, remained fixed while the inner particles, $\rho < \rho_T$, interact with each other and the wall particles and were allowed to move. (Here ρ is the distance from the center of the cylinder.)

The time evolution of the system was calculated by solving the equations of motion with the velocity form of the Verlet algorithm with a time step of 0.01 at high ($T \geq 1.0$) and 0.02 at low ($T \leq 0.8$) temperatures. To improve the statistics we simulated between 8 and 16 independent systems, each containing 1905 fluid particles and about 2300 wall particles. The tube length of 20.137 was chosen such that the average particles density is 1.2, the same value as used in the earlier simulations of the bulk. The temperatures investigated were T=2.0, 1.0, 0.8, 0.7, 0.6, and 0.55. The equilibration was done by periodically coupling the liquid to a stochastic heat bath. All data presented here was produced during a microcanonical run at constant energy and volume.

3. RESULTS

The analysis of the static properties of the confined system gave the expected results. Looking at the density profile in a plane perpendicular to the axis of the tube, normalized to its average value,

$$d_\alpha(\rho) = \left\langle \int_{interior} \sum_{i=1}^{N_\alpha} \delta \left(\sqrt{x_i^2 + y_i^2} - \rho \right) \right\rangle \cdot \left[\frac{N_\alpha}{V} \right]^{-1}, \text{ where } \alpha \in \{A, B\}, \tag{1}$$

we observe only a small dependence of d on the distance ρ from the center (Fig. 1). Due to the roughness of the surface the fluid particles can penetrate slightly into the wall. We can define a penetration radius ρ_p as the distance from the center of the tube at which there is almost no chance of finding a particle, namely the value of ρ were the density profile has decreased to 10^{-4} from its bulk value. For A particles we find
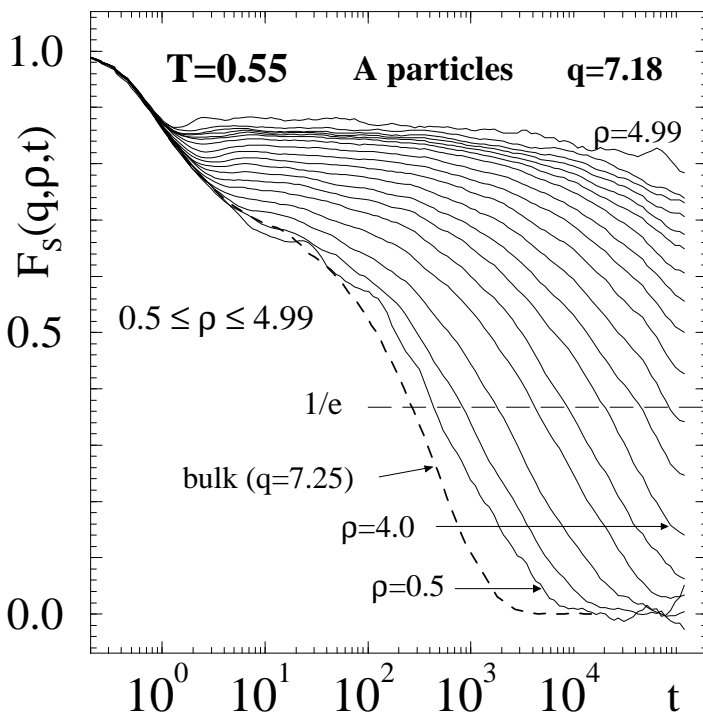
Figure 3. Time dependence of the self part of the intermediate scattering function for different values of ρ for A particles at T=0.55.

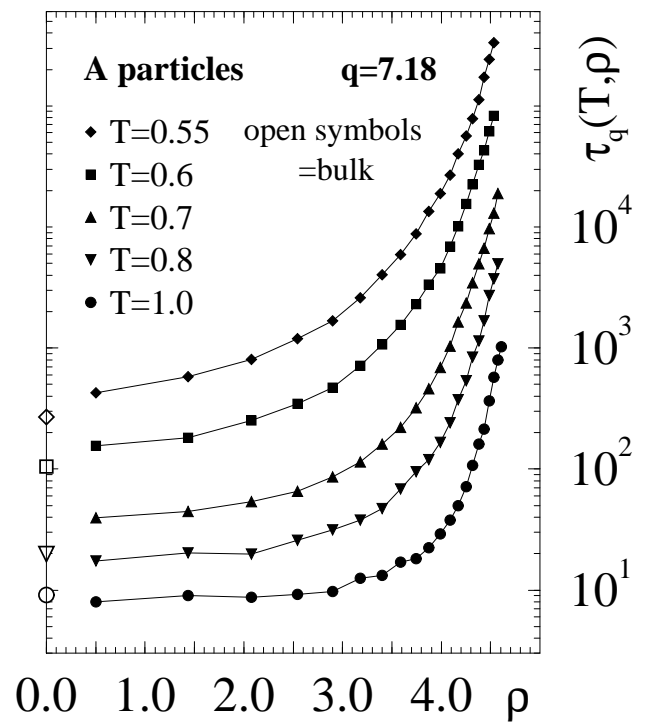**Figure 4.** ρ-dependence of the relaxation times $\tau_q(T, \rho)$ of $F_s(q, \rho, t)$, compared with the corresponding bulk values.

$\rho_A \approx 5.5 \pm 0.2$, and for the smaller B particles $\rho_A \approx 6.1 \pm 0.2$, values that depend only weakly on temperature below T=0.7. From the figure we see that the fluid has a tendency to form concentric layers, especially at low temperatures, but that this effect is only weak.

The radial distribution function in z-direction,

$$g^z_{\alpha\beta}(r) \propto \left\langle \sum_{i=1}^{N_\alpha} \sum_{\substack{j=1 \\ x_{ij}^2 + y_{ij}^2 < \mu^2}}^{N_\beta} \delta\left(r - |\vec{r}_i - \vec{r}_j|\right) \right\rangle, \quad \alpha \in \{A, B\} \ , \ \mu^2 = 0.5^2 \tag{2}$$

shows no strong deviation from its bulk behavior (Fig. 2). Even at the lowest temperature, T=0.55, there is only a small difference in peak positions and amplitudes between the bulk curve and the one for particles in the outer region, $\rho \geq 4.0$, of the tube. At high T this difference can hardly be seen. Similar results are obtained for AB- and BB-correlations and also the static structure factor is hardly affected by the confinement.

In contrast to this, the dynamical properties of the system change dramatically due to the confinement. All investigated dynamic quantities (mean squared displacement, intermediate scattering function, and van Hove correlation function) show a strong ρ-dependence. The following results were obtained by labeling a particle with its distance from the z-axis at time t=0, and analysing its dynamics as a function of its position. Fig. 3 shows the ρ-dependence of the self part of the intermediate scattering function,

$$F_s(q, \rho, t) = \langle \exp\left[i\vec{q} \cdot (\vec{r}(t) - \vec{r})\right] \cdot \delta\left(x^2(0) + y^2(0) - \rho^2\right) \rangle, \tag{3}$$

for A particles and $\vec{q}$ along the z-axis with modulus q corresponding to the maximum of the static structure factor for AA correlations at the lowest temperature investigated (T=0.55). While the relaxation of $F_s(q, \rho, t)$ in the center is similar to the one in the bulk, it becomes much slower with increasing ρ, i.e. on approach to the wall. The slowing down of the dynamics when approaching the wall exceeds more than three orders of magnitude. Since any particle tagged at time zero moves within a range of radii with different intrinsic relaxation times during the run, the averaged relaxation is more stretched than in the bulk, especially close to the wall, where the differences between relaxation times is large.

In order to investigate the ρ-dependence of the dynamics we define a characteristic ρ-dependent relaxation time $\tau_q(T, \rho)$ of the intermediate scattering function as the time at which it has decayed to e^{-1} of its initial value and compare these times. A quantitative analysis of the ρ-dependence of this relaxation times for the investigated temperatures below $T=1.0$ give the following results (Fig. 4). At higher temperatures particles in the inner region, $\rho \leq 2.0$, show almost bulk behavior before a strong increase in $\tau_q(T, \rho)$ becomes apparent for higher ρ. At low temperatures the presence of the wall affects the dynamics of the particles even in the center of the tube. The curves for all temperatures show an apparent divergence in the vicinity of the wall. The given statements above hold for A and B particles and also for different wave vectors.

Based on these observations we found an empirical law which is able to describe the ρ-dependence of the relaxation times of the intermediate scattering function. The data from Fig. 4 is described well by the functional form

$$\tau_q(T, \rho) = f_q(T) \exp\left[\Delta_q/(\rho_p - \rho)\right], \tag{4}$$

at least in the vicinity of the wall, i.e. for $\rho \geq 3.5$, which corresponds to half of the particles. In Eq. (4), the penetration radius ρ_p is determined as mentioned above from the static properties and depends only weakly on temperature. The quantity Δ_q depends on particle type and the value of q. The only temperature dependent quantity in this fit is the amplitude $f_q(T)$, which also depends on particle type and q. If we assume that in the supercooled state Eq. (4) holds for most of the particles, the slowing down of the system in the supercooled state is mainly characterized by the temperature dependence of the amplitude $f_q(T)$. More details on this will be discussed elsewhere [10].

4. SUMMARY

We have presented the results of a computer simulation of a simple glass former in a narrow tube. We find the relaxation times of the intermediate scattering function to be strongly dependent on the distance from the wall. We are able to describe this behavior by an empirical law predicting a divergence at $\rho = \rho_p$, where ρ_p is determined from static quantities. We see a gradual slowing down of the dynamics of the whole system, especially no immobile layer close to the wall, in agreement with experiments by Richert [11]. Note that we expect a similar slowing down of the dynamics in the vicinity of a wall also for other tube radii and even in a slit geometry, and that in the case of a narrow confinement, such as the one we investigated here, this slowing down will dominate the dynamics of the whole system.

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